

ALTERATION OF THE SURFACE PROPERTIES OF
STIBNITE AS REVEALED BY ADHESION
TENSION STUDIES

A DISSERTATION

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN
THE UNIVERSITY OF MICHIGAN

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CHARLES W. WALTON, JR.

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ALTERATION OF THE SURFACE PROPERTIES OF STIBNITE AS REVEALED BY ADHESION TENSION STUDIES

For adhesion tension studies, solids may be divided into two classes, hydrophilic solids which are wet more readily by water than by organic liquids, and hydrophobic solids which are wet more readily by organic liquids than by water.

Silica and oxides in general are hydrophilic. Carbon and various sulfides are hydrophobic. Quantitative experiments on Prussian blue indicate that it has non-selective wetting properties and is wet as readily by organic liquids as by water. Different hydrophilic solids show different degrees of preferential wetting by water, and different hydrophobic solids show different degrees of preferential wetting by organic liquids. In the present investigation a series of solids was sought whose wetting characteristics would cover the range from the extremely hydrophobic type to the extremely hydrophilic type. A major aim of this investigation was the correlation of the changes in free surface energy which occur when such a series of solids is wet by liquids.

Sulfides such as stibnite are slightly unstable at ordinary temperatures, and at slightly elevated temperatures they are readily oxidized. Preliminary tests showed that ordinary stibnite, Sb_2S_3 , was hydrophobic, though not so strongly hydrophobic as carbon. Samples of stibnite were therefore subjected to successive limited oxidations to determine whether the material so treated could be caused to change its properties, step by step, from a hydrophobic solid to a hydrophilic solid.

PREPARATION OF MATERIALS

A quantity of relatively pure stibnite was ground and carefully graded. Samples of this stibnite will be referred to as stibnite A. Other samples of stibnite were prepared by heating stibnite A to 170°C . for different lengths of time. The series of stibnites was as follows:

Stibnite A = Unheated, finely ground stibnite graded to 250 to 300 mesh and air floated. Mixed thoroughly in a rotating cylinder for 2 hours.

Stibnite B = Stibnite A heated 1 hour

Stibnite C = Stibnite A heated 2 hours

Stibnite D = Stibnite A heated 3 hours
 Stibnite E = Stibnite A heated 4 hours
 Stibnite F = Stibnite A heated 5 hours
 Stibnite G = Stibnite A heated 6 hours
 Stibnite H = Stibnite A heated 8 hours
 Stibnite I = Stibnite A heated 8 hours (400–420°C.) in a nitrogen atmosphere containing 0.7 per cent oxygen. This sample was graded to 250 to 300 mesh, but was not air floated.

Preliminary tests showed that stibnite I was hydrophilic and that each of the stibnites in the series with progressive degrees of oxidation was progressively less hydrophobic than stibnite A. It was observed also that if stibnite I were treated with hydrogen sulfide gas for a few minutes at a

TABLE 1
Adhesion tension data for water against different stibnites
 Water-air-stibnite system
 $S_3 = 72.08$ dynes per centimeter

STIBNITE	$r \times 10^{-4}$ CM.	P <i>grams per cm².</i>	$\cos \theta_{13}$	θ_{13}	A_{13} <i>dynes per cm.</i>
A	8.52	135	0.785	38°	56.5
B	8.52	137	0.794	37°	57.2
C	8.52	139	0.806	36°	58.1
D	8.52	144	0.836	33°	60.3
E	8.52	154	0.890	27°	64.2
F	8.52	159	0.922	23°	66.5
G	8.52	169	0.979	12°	70.5
H	8.52			0°	76.0*
I	11.1			0°	77.1*

* Values obtained from interfacial contact angle determinations.

slightly elevated temperature, it could be converted back into the hydrophobic type.

In addition to the stibnite powders, aluminum oxide was also used. It was graded to 300 to 350 mesh by sieving. The powder was treated twice with boiling hydrochloric acid (1:1) and allowed to stand in contact with the acid for several hours. It was washed six times with hot distilled water and was then washed twenty times with boiling distilled water while being filtered. It was dried at 110°C., then heated at 400° to 480°C. for 2 hours. The powder was thoroughly mixed, then heated at 510° to 530°C. for 8 hours and again mixed.

LIQUIDS

The water used was twice distilled and the accepted surface tension of 72.08 at 25°C. was used in all calculations for water.

The organic liquids used were very carefully purified and their surface

tensions and interfacial tensions against water were determined and used in all calculations.

METHOD AND APPARATUS

The displacement pressure cells and method used in this investigation for the determination of adhesion tension were the same as developed by

TABLE 2

Adhesion tension data for contact angle liquids against stibnites H and I

STIBNITE	LIQUID	$r \times 10^{-4}$ CM.	P	Θ_{12}	$\cos \Theta_{12}$	S_2	A_{12}
H	α -Bromonaphthalene	8.52	$\frac{\text{grams}}{\text{per cm}^2}$ 104	8°	0.988	$\frac{\text{dynes}}{\text{per cm.}}$ 44.00	$\frac{\text{dynes}}{\text{per cm.}}$ 43.5
I	α -Bromonaphthalene	11.1	73.5	25°	0.910	44.00	40.0
I	Acetylene tetrabromide	11.1	79.8	28°	0.885	49.07	43.4

TABLE 3

Comparison of adhesion tension data of several liquids as determined against stibnite A and stibnite I

LIQUID	STIBNITE A ($r = 8.52 \times 10^{-4}$ CM.)					STIBNITE I ($r = 1.11 \times 10^{-3}$ CM.)		
	Sur- face ten- sion	In- ter- fac- ial ten- sion	P	$\cos \Theta_{23}$	Ad- he- sion ten- sion	P	$\cos \Theta_{23}$	Ad- he- sion ten- sion
	$\frac{\text{dynes}}{\text{per cm.}}$	$\frac{\text{dynes}}{\text{per cm.}}$	$\frac{\text{grams}}{\text{per cm}^2}$		$\frac{\text{dynes}}{\text{per cm.}}$	$\frac{\text{grams}}{\text{per cm}^2}$		$\frac{\text{dynes}}{\text{per cm.}}$
1. Water.....	72.08	—	135	—	56.5	—	—	77.1*
2. Isoamyl alcohol.....	22.90	5.00	8.12	-0.679	59.9	5.70	0.621	74.0
3. <i>n</i> -Butyl acetate.....	24.06	13.17	23.0	-0.729	66.1	22.3	0.923	64.9
4. Benzene.....	28.22	34.31	52.3	-0.638	78.4	58.2	0.924	45.4
5. Acetylene tetrabromide.....	49.07	38.32	58.9	-0.642	81.1	79.8	—	43.4
6. α -Bromonaphthalene.....	44.00	41.57	68.2	-0.686	85.0	73.5	—	40.0
7. <i>n</i> -Heptane.....	19.80	49.40	69.9	-0.592	85.7	81.4	0.897	32.8

* Value obtained from interfacial contact angle determination.

Bartell and Jennings (3). The temperature was maintained constant in an air thermostat at $25^\circ\text{C.} \pm 0.05^\circ\text{C.}$

ADHESION TENSION AND CONTACT ANGLE MEASUREMENTS

From pressure of displacement measurements it was found that with progressive oxidation of the stibnite surface, the contact angle between water and solid decreased progressively. This is shown from the data presented in table 1. The adhesion tension values for water against all the solids except stibnite H and stibnite I were determined directly from the

solid-liquid-air displacement pressure data (4) and the values obtained ranged between 56.5 and 70.5 dynes per centimeter. Adhesion tension values for α -bromonaphthalene and acetylene tetrabromide against stibnite H and stibnite I were also determined directly. Having this latter

TABLE 4
Adhesion tension data of zero contact angle liquids against different stibnites
Water-organic liquid-stibnite systems

STIBNITE	$r \times 10^{-4}$ cm.	A_{13}	BENZENE				n-BUTYL ACETATE				α -BROMONAPHTHALENE			
			P	Θ_{23}	$\cos \Theta_{23}$	A_{12}	P	Θ_{23}	$\cos \Theta_{23}$	A_{12}	P	Θ_{23}	$\cos \Theta_{23}$	A_{12}
			<i>dynes</i> <i>per</i> <i>cm.</i>			<i>dynes</i> <i>per</i> <i>cm.</i>	<i>dynes</i> <i>per</i> <i>cm.</i>			<i>dynes</i> <i>per</i> <i>cm.</i>	<i>dynes</i> <i>per</i> <i>cm.</i>			<i>dynes</i> <i>per</i> <i>cm.</i>
A	8.52	56.5	52.3	130°	-0.638	78.4	23.0	137°	-0.729	66.1	68.2	134°	-0.686	85.0
B	8.52	57.2	46.5	124°	-0.566	76.6	22.0	134°	-0.697	66.4	60.2	127°	-0.605	82.4
C	8.52	58.1	42.9	121°	-0.522	76.0	18.5	126°	-0.587	65.8	55.2	124°	-0.555	81.2
D	8.52	60.3	29.4	111°	-0.358	72.6	13.0	114°	-0.414	65.8	38.8	113°	-0.389	76.4
E	8.52	64.2		>90°				>90°				>90°		
F	8.52	66.5		<90°				<90°				<90°		
G	8.52	70.5	37.0	63°	-0.452	55.0	13.1	65°	-0.417	65.0	38.4	68°	-0.386	54.5
H	8.52	76.0	69.4	32°	-0.845	47.0	26.7	31°	-0.854	64.8	77.6	39°	-0.780	43.5
I	11.1	77.1	58.2	22°	-0.924	45.4	22.3	23°	-0.923	64.9	68.0	27°	-0.891	40.0

Interfacial angle <90°—water displaces organic liquid.

Interfacial angle >90°—organic liquid displaces water.

TABLE 5
Adhesion tension data for several liquids against aluminum oxide
 $r = 8.42 \times 10^{-4}$ cm.

LIQUID	P	$\cos \Theta_{23}$	ADHESION TENSION
	<i>grams per cm².</i>		<i>dynes per cm.</i>
1. Water.....	—	—	76.7*
2. Isoamyl alcohol.....	6.77	0.556	73.9
3. <i>n</i> -Butyl acetate.....	29.4	0.924	64.5
4. Benzene.....	76.7	0.924	45.0
5. Acetylene tetrabromide.....	104	0.878	43.0
6. α -Bromonaphthalene.....	97	0.884	40.1
7. <i>n</i> -Heptane.....	105	0.877	33.4

* Value obtained from interfacial contact angle determination.

data, the adhesion tension value of water against each of the two solids was obtained indirectly from liquid-liquid-solid displacement pressure data by using in turn each of these organic liquids and water against each of the stibnites. Stibnite H gave an adhesion tension value with water of 76.0 dynes per centimeter, and stibnite I gave a value of 77.1 dynes per centimeter (table 1).

A comparison of adhesion tension data of several liquids against stibnite A and stibnite I may be made from the data given in table 3. Adhesion tension data for a series of liquids against the different stibnites are given in table 4. Data for a series of liquids against aluminum oxide are given in table 5.

CORRELATION OF ENERGY CHANGES OCCURRING ON THE WETTING OF SOLIDS

Bartell and Osterhof (1) had observed that when the adhesion tension values of carbon and silica were compared, the order of increasing adhesion

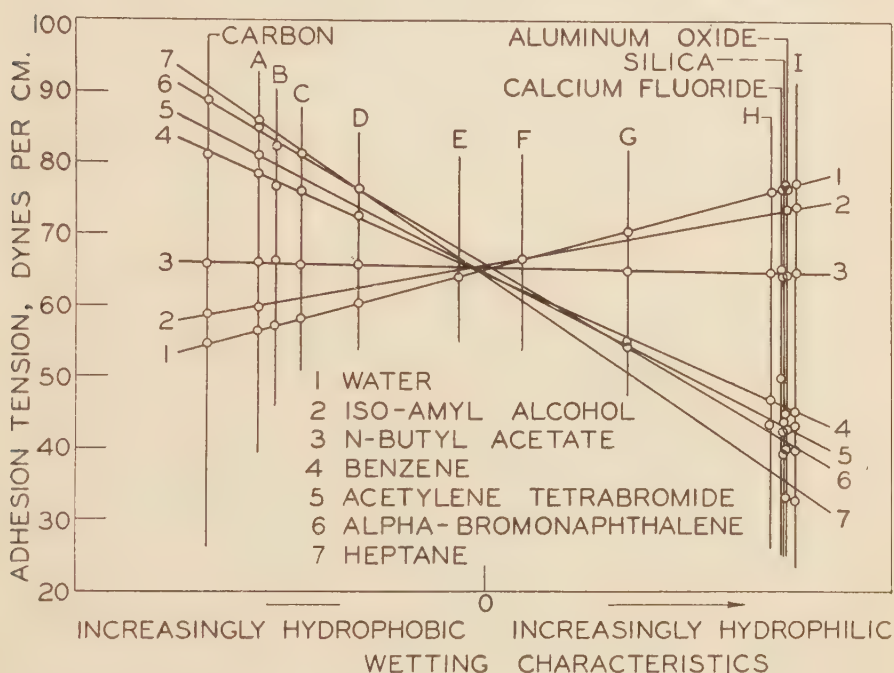


FIG. 1

tension values for the one solid against a series of liquids was just opposite to the order of increasing adhesion tension values of the other solid against this same series of liquids. They suggested (5) that the results might be correlated diagrammatically so as to show linear relationships for the adhesion tension values of a series of liquids against a series of solids when these values are plotted against the wetting characteristics of the solids. This proposed relationship had but little significance at the time, inasmuch as no adhesion tension data were available for systems whose wetting characteristics were intermediate between those of carbon and silica, with the exception of qualitative data on Prussian blue which showed that it was

wetted to practically the same degree by all the liquids used. Its wetting characteristics would then place it near the middle of such a diagram.

In this proposed diagram the adhesion tension values of the different liquids (i.e., liquids No. 1, 2, 3, 4, and 5) were to be plotted as ordinates and wetting characteristics, in arbitrary units, as abscissae. Such a diagram was constructed and an attempt was made to place the values for the different stibnites on it.

The adhesion tension values for carbon and silica were placed in vertical positions at the ends of the wetting characteristics axis. A straight "tie line" was drawn to connect the adhesion tension values for water against these solids. The positions for the adhesion tension values of water against the different stibnites were located upon this tie line and a vertical line drawn through each point. It was a fact of great interest that the adhesion tension values for the different liquids against each of the different stibnites were found to correspond to the ordinates of points on the "tie lines" set up between carbon and silica where these "tie lines" were intersected by the vertical lines. These relationships are shown in figure 1.

It may be noted that heat treatment of the original stibnite A for 1-hour and 2-hour periods had but little effect on the adhesion tension values. As the time of heating was increased, the surface energy changes were found to be greater and the state of the solid surface to have progressed toward that of the hydrophilic solids.

The adhesion tension values for water and for isoamyl alcohol against the solid were observed to have increased in a linear manner with increase of surface oxidation. The adhesion tension values for heptane, benzene, α -bromonaphthalene, and acetylene tetrabromide were observed to have decreased in a linear manner with increased oxidation. The adhesion tension of *n*-butyl acetate was observed to have remained at practically the same value for all samples of stibnite regardless of degree of oxidation. This liquid appeared to wet all the solids to practically the same degree.

The adhesion tension data for other solids against the same series of liquids were collected and also plotted (figure 1). The similar wetting tendencies of the hydrophilic solids should be noted.

It will be seen that as the middle of the diagram is approached from either side, the difference in energy levels becomes less and less, hence the degree of selective wetting of the different solids by given liquids becomes correspondingly less and less. At the center of the diagram the "tie lines" have almost a common point of crossing. If this were actually a common point, it would represent a "point of non-selective wetting." The interfacial contact angle at this point would be exactly 90° . If a solid possessed surface properties represented by this position on the diagram, it would be wetted equally well by all liquids (at least by liquids of the type of those studied). At this "point of non-selective wetting" all interfacial energy

levels would be the same, and hence the adhesion tension values of all liquids against the solid would be the same. In a displacement pressure cell there would be no displacement of liquid by liquid (organic liquid-water) in either direction. That liquid which wetted the powder first would not tend to be displaced by the second liquid. Stibnites E and F fall near the middle of the diagram. The difference in energy levels of the different liquids against these solids was so low that accurate measurement of them was not possible. Accordingly adhesion tension values of the organic liquids against these solids were not determined. Our only criterion of their surface condition (i.e., the hydrophilic or hydrophobic nature) was obtained through the adhesion tension value of water, which was determined by measurement of the solid-water-air contact angle.

In passing outward in either direction from this region of non-selective wetting, the difference in energy levels becomes greater and greater. The ease with which one liquid will displace another from the solid becomes correspondingly greater.

QUALITATIVE TESTS FOR THE DETERMINATION OF RELATIVE DEGREE OF WETTING

When the quantitative work of the relative degree of wetting had been practically completed, it was decided to make some qualitative tests which might give further and optically convincing evidence that the surface properties of the original stibnite had been altered in a definite and regular manner. It was hoped that those tests might be indicative of the practical importance of the data obtained. Two series of qualitative tests were run. One series will be designated as the "drop on powder test" and the other as the "degree of packing upon settling test."

Drop on powder test

In the first series of tests a drop of water was placed on smoothed out samples of the different powdered stibnites. When placed on stibnite A the drop appeared to give a large contact angle against the powder and showed no tendency to disappear into the powder, but persisted until the water evaporated. When the stibnites with the progressively altered surface characteristics were tested, the drops of water which remained upon them were progressively smaller and the contact angles formed likewise were progressively smaller. When water was placed on stibnites H and I no drops formed, the angle of contact of water against the solid was zero, the water wetted the stibnite completely and disappeared entirely into the powder. The results obtained in this series of tests were what one might expect to obtain with a series of powders with surface properties ranging from strongly hydrophobic to strongly hydrophilic.

Degree of packing on settling test

In the second series of tests the powdered solid was suspended in liquid media and observations were made of the degree of packing of the powder on settling. This test was suggested by work previously done on "liquid absorption" (1, 2). Altogether six separate experiments were run.

The six experiments were as follows: (1) water, (2) *n*-butyl acetate, and (3) α -bromonaphthalene, with each of the nine different stibnites, and (4) stibnite A, (5) stibnite E, and (6) stibnite I with each of the seven different liquids.

In each of the experiments 10 g. of powder, together with 7 cc. of liquid, was put into each of a series of test tubes of uniform diameter, thoroughly

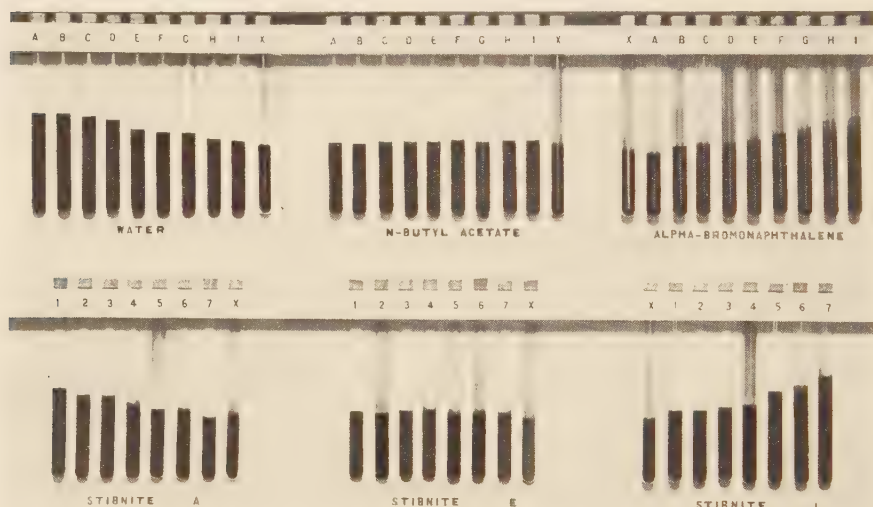


FIG. 2

mixed, and allowed to settle. The stibnite samples were similar to, but not the same as, those that were used in the adhesion tension work. The tests were made upon finely ground, ungraded stibnite which had been subjected to the same treatment as the previously described samples of graded powders. The symbols used to indicate the different heat treatments are the same as those used for the graded powders. The liquids used were numbered as for the adhesion tension experiments, viz., 1 = water, 2 = isoamyl alcohol, 3 = *n*-butyl acetate, 4 = benzene, 5 = acetylene tetrabromide, 6 = α -bromonaphthalene, and 7 = *n*-heptane. The test tubes labeled X contain 10 g. of stibnite, but no liquid medium.

A photograph of the tubes, figure 2, clearly presents the results obtained. The photograph was taken about a week after the settling test was started.

After four months the heights of the settled powders were practically unchanged. A similar set of settling tests made with finely divided silica (Silex) gave similar effects upon settling and the heights of the different powders have remained unchanged for a period of over two years.

The results obtained in each of the six experiments mentioned may be briefly summarized in the statement that the degree of packing of the powder upon settling is greatest in that liquid against which it possesses the greatest adhesion tension and is progressively less in those liquids against which it has a progressively lesser adhesion tension.

The experiments showed conclusively that the surface properties of the stibnites were altered by the simple heat treatment. They showed that it is possible to alter greatly the preferential wetting properties of certain solids; that one can cause surfaces to function either as hydrophobic or hydrophilic surfaces. Moreover, it is possible to reduce surfaces to a condition in which they show no selective wetting tendency, that is, they are preferentially wetted neither by water nor by organic liquids.

In the present paper we shall make no attempt to discuss the character of the different surfaces studied, nor of the theories pertaining to the change in surface properties. It may be of interest to mention that the appearance of the surfaces was unaltered, the particle size of the powder was unaltered, and the pore radii formed with each sample of the different graded powders were the same. This work is being considerably extended in our laboratories and we expect to present more comprehensive generalizations in the near future.

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